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COMMERCIAL CREOSOTES

WITH SPECIAL REFERENCE TO PROTECTION OF WOOD FROM DECAY.

BY

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COMMERCIAL CREOSOTES WITH SPECIAL REFERENCE TO PROTECTION OF WOOD FROM DECAY

PURPOSE OF THE STUDY.

The aim of this circular is to tell the more important sources of wood-preserving creosotes, the methods used in their production, their general properties, and the quality, price, and quantity of the creosotes annually consumed in this country. As a whole, it is intended more for the consumer who is unfamiliar with the various products sold as creosote than for the chemist or manufacturer, who is well informed on their technical qualities.

For some years the Forest Service has conducted investigations regarding the properties and methods of analysis of various creosotes and the more important of the results secured have been published.[1] This work has been, and will be, continued. The major part completed at the present time, which is embodied in this report, is an investigation of the quality and prices of the creosotes available commercially. For this study, samples of creosote were collected from manufacturers and dealers throughout the country and were critically analyzed. At the same time, information was secured from the dealers as to prices, and statistics were collected on the annual consumption.[2]

Further and more extensive investigations are now under way at the Forest Products Laboratory maintained in cooperation with the University of Wisconsin, at Madison. Samples of a large number of authentic coal tars, oil tars, and wood tars have been collected, from which creosotes are being distilled and critically analyzed and examined. At the same time experiments are being conducted to determine the comparative efficiency of various creosotes as wood preservatives. It is hoped that through this work the wood-preserving value of any creosote can be foretold with a fair degree of certainty for any specific condition of service, simply by a knowledge of its physical and chemical characteristics without regard to its source or method of production.

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[1] Forest Service Circular 80, Fractional Distillation of Coal-Tar Creosote, by Arthur L. Dean and Ernest Bateman; Circular 98, Quantity and Character of Creosote in Well-Preserved Timbers, by Gellert Alleman; Circular 112, Analysis and Grading of Creosotes, by Arthur L. Dean and Ernest Bateman.

[2] Mr. H. F. Weiss, assistant director, forest products laboratory, planned the work and collected the samples of creosote. Mr. Ernest Bateman, chemist in forest products, furnished much of the information and directed the analysis of the samples. Mr. C. H. Teesdale, assistant engineer in forest products, actually conducted the analyses.

Because of the present lack of knowledge of the properties of all of the various creosotes which may be produced, the terms, definitions, and classifications proposed and used in this publication are subject to criticism and possible future modification. The limits described for the several classes are based on physical and chemical properties possessed by creosotes produced from the sources, or by the methods specified. It is possible that creosotes from other sources may be found to possess similar properties, yet no other method which will indicate the source more satisfactorily than that discussed in this publication is now known to the Forest Service.

DEFINITIONS.

Much misunderstanding exists as to the meaning of the term "creosote." It is defined by the Standard Dictionary as "a colorless to yellowish oily liquid compound consisting of a mixture of phenols distilled from wood, and having a smoky odor and burning taste. It is a powerful antiseptic and is used for the preservation of timber, meat, etc.; called also oil of wood tar and oil of smoke." Allen, in his Commercial Organic Analysis, says: "The name 'kreosot' was first applied by Reichenbach, in 1832, to the characteristic antiseptic principle contained in wood tar. Carbolic acid was discovered soon after by Runge in coal tar, and was long confused with the wood-tar principle; and the crude carbolic acid from coal tar is still known as 'coal-tar creosote.' Somewhat similar products are now obtained from other sources, so that much confusion has arisen. The term 'creosote,' when used without qualification, ought to be understood as signifying the product from wood tar, but it is better to describe Reichenbach's body as 'wood-tar creosote,' and employ the unqualified word 'creosote' in a generic sense as meaning the mixed phenols and phenoloid bodies obtained from wood tar, coal tar, blast-furnace tar, shale oil, bone oil, or other sources."

In its original meaning, therefore, the term "creosote" was applied to a product obtained from wood, and the term is still used thus in pharmacy, and refers to a refined product derived from the destructive distillation of beech or other hardwood. However, with the development of both the wood-preserving and the coal-tar industries, the term "creosote oil," frequently abbreviated to "creosote," gradually came to be applied to the heavy distillates from coal tar, and the use of the term has become more and more extended until, at the present time, it is commonly used in referring to the distillates heavier than water from any tars or tarlike substances, and is even erroneously used to cover products containing admixtures of undistilled tar or pitch. As a result of this lax use of the word it conveys but little to those conversant with the subject and is confusing to those unfamiliar with commercial practice. More specific terms are evidently needed to properly differentiate between the various creosotes. The most useful classification from the wood preserver's point of view would be one based upon the merits of the various products, but lack of sufficient data renders this impossible. The only practical classification at present must be based upon the source and method of production. The following terms and definitions are suggested, and will be used in this publication:

1. *Creosote* is a distillate heavier than water obtained by the distillation of a tar or a tarlike substance.

2. *Coal-tar creosote* is a creosote derived from coal tar produced by the destructive distillation of coal at a temperature high enough to produce a tar consisting, for the most part, of hydrocarbons of the aromatic series.[1]

3. *Oil-tar creosote*[2] is a creosote derived from oil tar. This tar may be obtained from the destructive distillation of petroleum in a gas retort, producing oil gas as a main product and oil-gas tar as a by-product, or by the cracking of gas oil in the carburetor of a water-gas plant producing carbureted water gas as a main product and carbureted water-gas tar as a by-product.

4. *Wood-tar creosote* is a creosote derived from a tar produced by the destructive distillation of wood.

5. *Mixed creosote* is a creosote produced by mixing other material with a given creosote, such as another creosote, pitch, undistilled tar, or petroleum, or it may be secured by the distillation of a mixture of two or more tars or tarlike substances. In view of the similarity between certain mixed creosotes and creosotes obtained by the distillation of coal tar, produced at temperatures sufficiently low to permit the production of hydrocarbons of the paraffin series, these latter distillates are also classed under this heading. The terms "mixed coal-tar creosote," "mixed oil-tar creosote," and "mixed wood-tar creosote" may be used according to the character of the material which predominates in the mixture.

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[1] Creosote secured from coal tar produced at sufficiently low temperature to permit the production of hydrocarbons of the paraffin series might also be included under the name of coal-tar creosote, but in view of the paraffin hydrocarbons it is classed in this publication as mixed coal-tar creosote.

[2] Inasmuch as the derivatives of oil-gas tars and water-gas tars contain no phenoloid bodies, the use of the term "creosote" in this connection might, from a purely technical standpoint, be considered erroneous. However, the term is used commercially at the present time in this connection, and a careful consideration of the various definitions used in this publication should prevent any misunderstanding.

PRODUCTION OF CREOSOTES.[1]

SOURCE OF TARS.

Although there are a variety of tars from which creosotes may be produced, the most important commercial ones may be classified as coal tars, oil tars, and wood tars. The sources and general methods of production of these tars are as follows:

Coal tars.

The important coal tars are derived chiefly from two sources: The destructive distillation of bituminous coal at high temperatures and the combined distillation and combustion of bituminous coal at comparatively low temperatures. The first, which furnishes by far the greater proportion of the total supply, is produced in the manufacture of coke and gas in by-product retorts and gas-house plants. Bituminous coal is destructively distilled at temperatures varying from 1,500° F. to 3,000° F., until the charge has been reduced to coke. During the process the ammoniacal liquor and tar are separated from the generated gases by condensation and washing. The tars naturally vary in their properties according to the character of the coal, and of the retorts, and according to the temperatures used. These factors in turn are largely dependent upon which of the two main products, gas or coke, is primarily desired; tar acids, however, are always present in the tars and usually the temperatures are sufficiently high in both cases to produce tars consisting largely of hydrocarbons of the aromatic series.

Coal tars produced at relatively low temperatures differ from those produced at higher temperatures in the character of their hydrocarbons. Since the temperatures are not high enough to transform all of the hydrocarbons to the aromatic series, the tars contain, to a greater or less extent, hydrocarbons of the paraffin group. Tars secured from blast furnaces using bituminous coal as fuel and from the Mond producer plants, where bituminous coal is used in the manufacture of gas for power purposes, are representative of this group. The production of such tars, however, is not extensive in this country.

Oil tars.

Of the oil tars, that produced in the manufacture of water gas is by far the most important in its relation to the manufacture of creosote. The method of production is, in general, as follows: The "generator" is charged with coke or anthracite coal, which is burned by the aid of an air blast to a cherry red. The hot gases so formed are passed through the "carbureter" and "superheater," which consist of vertical cylindrical chambers filled with a checker work of fire brick. After these bricks are heated to the proper temperature the air blast is discontinued and steam is blown into the generator. The gases formed by the contact of the steam with the hot coke or coal pass into the carbureter, into which petroleum "gas oil" is sprayed at the same time. This oil is partially cracked by the high temperature of the fire brick and combines with the gases from the generator to increase their illuminating power; the process of cracking continues through the superheaters. The gas is then passed to the condensers and washers, where tar is condensed and collected. This tar differs in its constituents from coal tar produced in the by-product coke ovens and gas retorts both in the absence of tar acids and in the presence of hydrocarbons of the paraffin series; usually, however, the quantity of paraffin hydrocarbons present is comparatively small.

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[1] Creosotes consist of complex mixtures of organic compounds, which may, however, be grouped into a comparatively few classes distinguished by their characteristic physical and chemical properties. For a more complete discussion the reader is referred to any standard textbook on organic chemistry.

Some oil tar also is produced by the destructive distillation of crude petroleum in the manufacture of oil gas. In tars from this source the quantity of paraffin hydrocarbons present is generally much greater than in that produced in the manufacture of carbureted water gas.

Wood tars.

Wood tar is produced in a manner somewhat similar to that in which by-product coal tar is formed. Wood is destructively distilled in retorts, and charcoal is produced, together with gas and a liquid distillate which consists largely of pyroligneous acid and a product called crude tar. The tar and acid are separated by settling and by distillation. Wood tars are quite different from coal tars and contain, in particular, less of the aromatic hydrocarbons.

DISTILLATION OF CREOSOTE FROM TARS.

From any or all of the foregoing tars, either alone or in mixture, creosote may be produced. The general process of manufacture is similar in all cases. The tar is distilled in a metal retort or still and the vapors are condensed and collected. Those distillates which are heavier than water form the true creosotes used in wood preservation. The temperatures at which the creosotes are obtained vary greatly, but generally lie between about 200° and 360° C. The actual temperatures in each case depend largely upon the character of the residue desired. In the United States the manufacture of creosote from coal tar is generally secondary to the manufacture of soft pitch; and in such cases the maximum temperature during the distillation is comparatively low. In Europe, on the other hand, coal tar is distilled largely for the production of the coal-tar dyes, and the distillation is carried to higher temperatures. The creosote, therefore, contains a relatively greater amount of the higher boiling constituents than the American product.

As already stated, pitch, undistilled tar, or other similar materials are frequently mixed with a creosote, and while such mixtures are sometimes sold as creosotes, the term is improperly applied except as it relates to the distilled product.

GENERAL REQUIREMENTS OF WOOD-PRESERVING OILS.

The value of any creosote as a preservative against decay is fundamentally dependent upon its ability to prevent the development of wood-destroying fungi. This prevention may be accomplished in either of the following ways:

1. By introducing a material sufficiently poisonous to wood-destroying fungi to prevent their development.
2. By introducing a material which will sufficiently exclude moisture or air to reduce the amount of either below that required by the fungi for their development.

In the past the creosotes which have been successful have generally possessed, at least to some extent, both of these properties; but the first is generally considered the more essential. In recent years, however, there has been some tendency to use materials not markedly antiseptic, but primarily intended to exclude moisture. As yet, however, it has not been completely demonstrated, nor generally accepted, that a product can be obtained to fullfil entirely the second requirement.

Aside from these considerations, it is of course essential that the creosote be of such a nature as to remain in the wood for the desired period of protection. In this connection its relative solubility in water and its volatility are important. However efficient it may be in poisoning the food supply or preventing the absorption of moisture, if it will not remain in the wood with a considerable degree of permanence, its ultimate value will be small. Where the treated wood is to be placed in wet situations or under water, as in the case of piling, a soluble preservative is inefficient; and a volatile preservative is especially unsuited for timbers exposed to the air in warm climates.

The relative ease with which a preservative can be injected is of much importance in wood-preserving operations; for this reason a product which is not sufficiently fluid at temperatures which can be conveniently used at commercial treating plants is undesirable. The presence of free carbon is known to decrease the penetrance of creosote and for this reason is objectionable.

COMPOSITION AND PROPERTIES OF CREOSOTES.

The complexity of the many hydrocarbons and their derivatives which may be produced in the destructive distillation of coal, oil, and wood, makes it impossible to state precisely the nature of the various constituents of all creosotes. However, they may be broadly divided into two classes, compounds of the aromatic series and compounds of the paraffin series. The characteristic difference between the two lies in the greater chemical activity of the former. Coal-tar creosote consists almost wholly of aromatic compounds, and the long period of successful use of such creosote has led to the general feeling that these constituents are the more desirable.

The compounds of the aromatic series may be divided into three groups, as follows: (1) "Light oils," which distill below 205° C. and consist largely of phenols and cresols, or tar acids; (2) naphthalenes, which distill between approximately 205° and 255° C.; and (3) constituents of an anthracene nature distilling above 255° C, which will be referred to collectively as "anthracenes." Some or all of these are found in most creosotes.

Of these constituents the tar acids possess the highest antiseptic properties; they are, however, soluble in water and are more volatile than the other constituents. The naphthalenes and anthracenes are neither so antiseptic nor so volatile as the tar acids and are practically insoluble in water. There is much discussion as to the relative value of these different constituents, but, largely as a result of experience, the presence of tar acids is believed by many to be essential. While a large proportion of naphthalene is sometimes advocated, particularly for the preservation of piling, a reduction in the quantity of this constituent, with a corresponding increase in the amount of anthracenes, is believed to increase the value of a creosote for general purposes.

COAL-TAR CREOSOTES.

Figure 1[1] shows graphically the derivation and general composition of coal-tar creosote. The relative quantity of tar acids, naphthalenes, and anthracenes will of course vary according to the character of the tar and the temperatures used during its distillation, but generally the tar acids present will not exceed 5 per cent, the naphthalenes will comprise from 15 to 50 per cent, and the anthracenes will comprise the remainder. As previously defined it contains practically no paraffin hydrocarbons. The creosote as a whole is antiseptic, insoluble in water, and somewhat volatile; it is sufficiently free from "free carbon," and fluid enough at temperatures used in commercial treating plants, to offer no great resistance to entrance into the wood.

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[1] In figs. 1 and 2, and Table 1, the term "solid at room temperature" (20° C.) is used in describing the condition of certain of the fractions distilled from creosote, when, at the ordinary temperature of a room, they retained their position in the receiving flask when vigorously shaken.

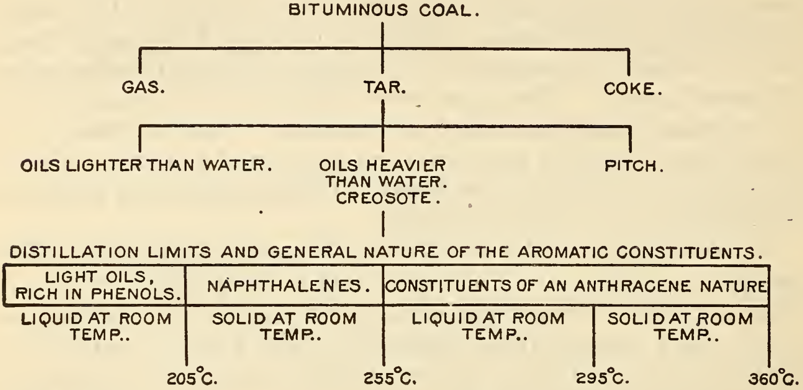

FIG. 1.—Derivation and general composition of coal-tar creosote.

WATER-GAS-TAR CREOSOTES.

Of the oil-tar creosotes, that from water-gas tar is practically the only one used for wood preservation. Figure 2 illustrates its derivation and general composition. This creosote is no more volatile nor soluble in water than coal-tar creosote, contains no "free carbon," and offers no marked resistance to entrance into the wood. In fact, water-gas-tar creosote may be produced which on fractional distilla-

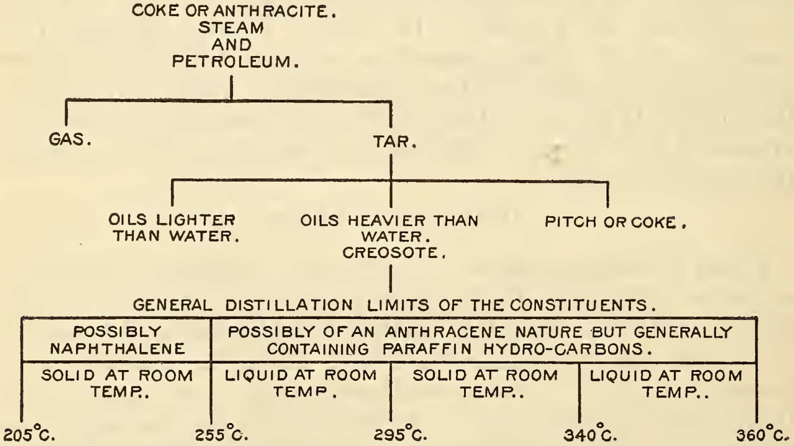
COKE OR ANTHRACITE. STEAM AND PETROLEUM.
GAS.
TAR.
OILS LIGHTER THAN WATER.
OILS HEAVIER THAN WATER. CREOSOTE.
PITCH OR COKE.
GENERAL DISTILLATION LIMITS OF THE CONSTITUENTS.
POSSIBLY NAPHTHALENE
POSSIBLY OF AN ANTHRACENE NATURE BUT GENERALLY CONTAINING PARAFFIN HYDRO-CARBONS.
SOLID AT ROOM TEMP.
LIQUID AT ROOM TEMP.
SOLID AT ROOM TEMP..
LIQUID AT ROOM TEMP..
205°C.
255°C.
295°C.
340°C.
360°C.

FIG. 2.—Derivation and general composition of water-gas-tar creosote.

tion will display a great similarity to coal-tar creosote. There is a difference, however, in the constituents of the two creosotes, as shown by the difference in certain physical properties of fractions distilled from them at equal temperatures. Furthermore, water-gas-tar creosote is distinctive in the absence of phenols and cresols, and usually in the presence of hydrocarbons of the paraffin group; it is not so antiseptic as coal-tar creosote.

WOOD-TAR CREOSOTES.

Of the wood-tar creosotes, that most used in the past has been secured from resinous woods. The derivation of such creosotes is illustrated in figure 3. Lack of authentic data prevents even a general statement as to its constituents, but the proportion of tar acids and volatile constituents is generally greater, and of naphthalene and anthracene much less, than in the coal-tar creosotes. Wood-tar creosotes have been used to some extent as wood preservatives for many years, but partly as a result of their comparatively high cost and limited production and partly through lack of authentic data regarding their efficiency, they do not rank in importance with the other creosotes.

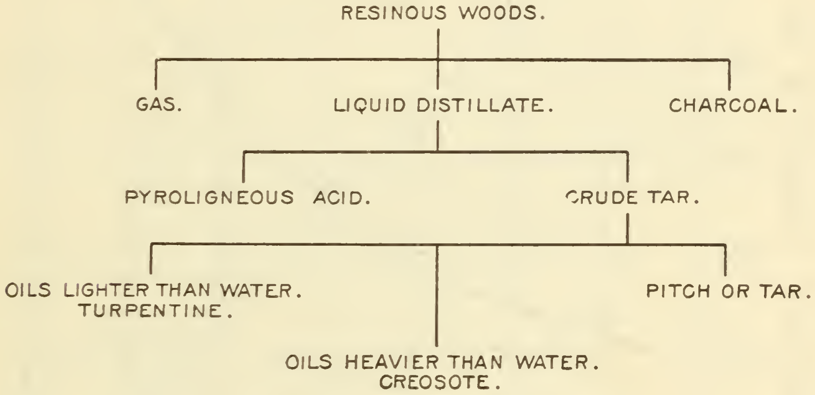

FIG. 3.—Derivation of wood-tar creosote from resinous woods.

MIXED COAL-TAR CREOSOTES.

A large part of the creosote produced in this country falls into the class of mixed coal-tar creosote. Some is made by the mixture of undistilled coal tar, or oil tar, or pitch, with coal-tar creosote; some is produced by the partial distillation and combustion of bituminous coal at comparatively low temperatures; and some is secured through the manufacture of soft pitch when coal tar and water-gas tar are distilled in admixture. The nature of all mixed coal-tar creosotes can not be described, because their constituents and relative merits as wood preservatives vary in each case according to the materials used in their production and preparation. Admixtures of undistilled tar or pitch containing free carbon will, however, tend to decrease the penetrance of the creosote, while the admixture of products which contain appreciable amounts of constituents of the paraffin series will doubtless affect in some measure the antiseptic properties of the creosote.

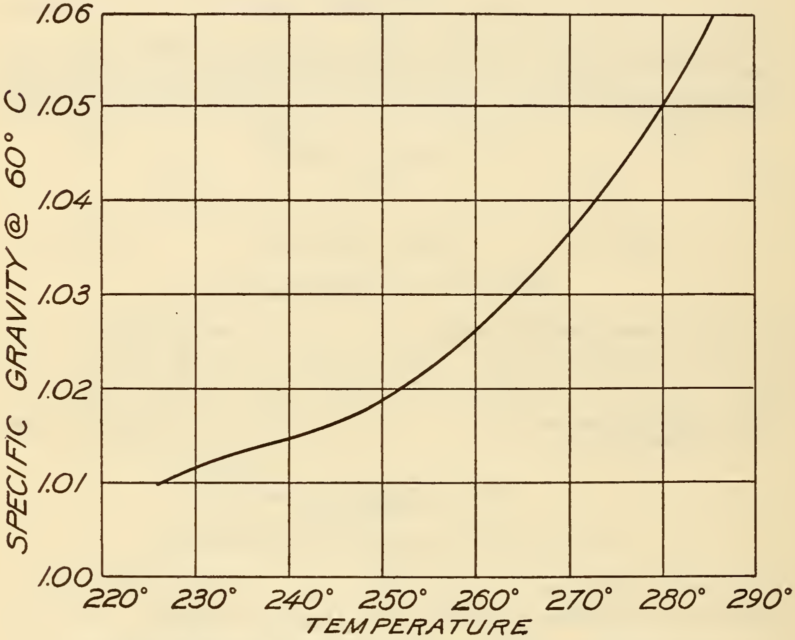

FIG. 4.—Lower limits for specific gravities of fractions from coal-tar creosote.

DISTINCTIVE PROPERTIES OF COAL-TAR CREOSOTES AND MIXED COAL-TAR CREOSOTES.

Whatever may be the individual opinion as to the merits of the various creosotes as wood preservatives, and no matter what creosote may be selected for use, it is obvious that the consumer ought to have some means of determining the source and nature of the material which he purchases. The Forest Service has not as yet sufficiently investigated all creosotes to permit a definite correlation of their physical and chemical properties with sources and methods of production; but certain characteristic properties of authentic coal-tar creosotes and mixed coal-tar creosotes, from several sources, have been determined with a considerable degree of certainty.

The more important points to be noted are:[1]

1. In the fractional distillation of the coal-tar creosotes the percentages of distillate coming over between the same temperatures, although varying widely for different creosotes, fell within fairly definite limits.

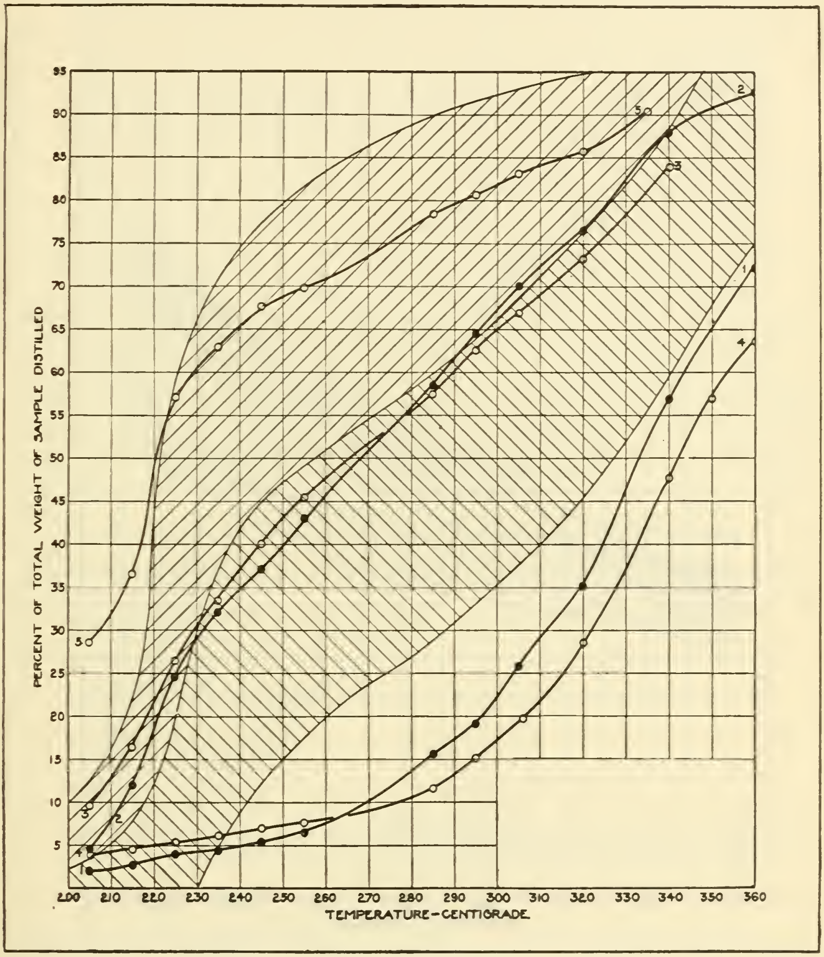

FIG. 5.—Fractional distillation curves for samples classed as coal-tar creosotes (classes 1 and 2).

2. With the coal-tar creosotes the fractions distilling above 320° C. did not melt at a temperature as low as 60° C., while similar fractions from creosotes with which petroleum products, such as water-gas-tar

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[1] These are discussed in Forest Service Circular 112, Analysis and Grading of Creosotes, by A. L. Dean and E. Bateman. The method of analysis used in these investigations, and described in Circular 112, is reprinted in the appendix to this publication.

creosote or the undistilled tar had been mixed, generally melted at that temperature.

3. With certain of the mixed coal-tar creosotes secured from coal tar produced by the combined distillation and combustion of bituminous coal at comparatively low temperatures the proportion of tar acids was high as compared to that from the coal-tar creosotes.

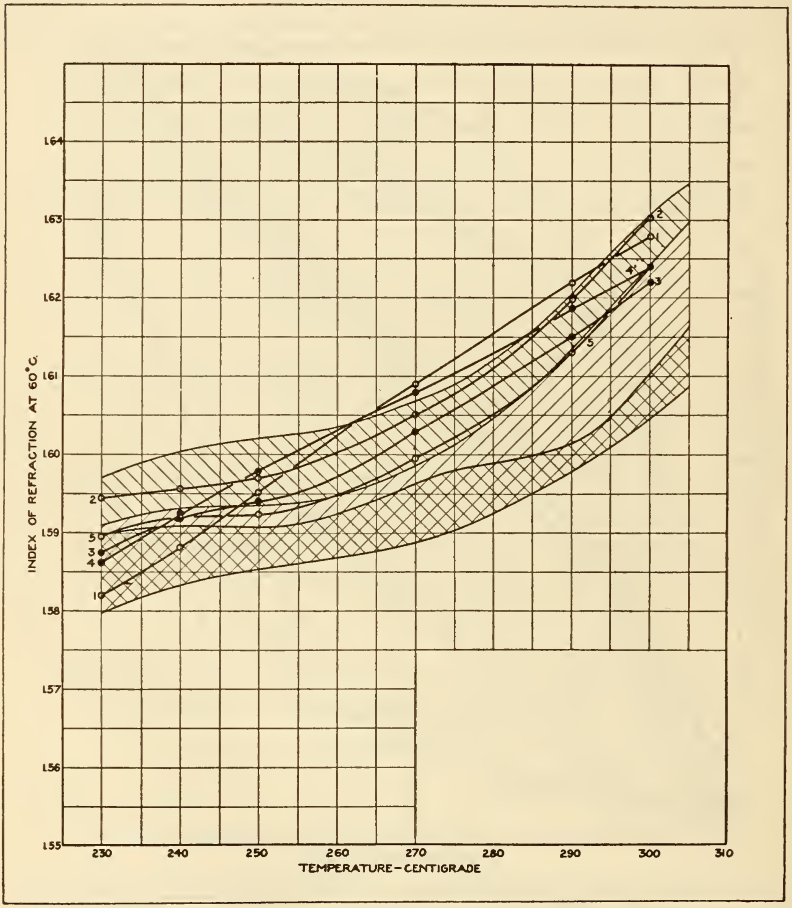

Fig. 6.—Index of refraction curves for samples classified as coal-tar creosotes (classes 1 and 2).

4. The most constant and serviceable physical properties were the index of refraction and specific gravity of certain of the fractions. These properties of fractions distilling between the same temperature limits were uniformly higher for the coal-tar creosotes, or those rich in aromatic hydrocarbons, than for those containing paraffin constituents. As a rule, the greater the quantity of paraffin hydrocar-

bons present in the fraction the lower the index of refraction and the specific gravity.

5. The most satisfactory chemical test was the "sulphonation test." The residues from the sulphonation test were larger as the quantity of paraffin hydrocarbons in the creosote increased. This is to be expected, because, with the exception of a possible oily residue, which is readily soluble in caustic alkalies, there is no residue from aromatic hydrocarbons alone.

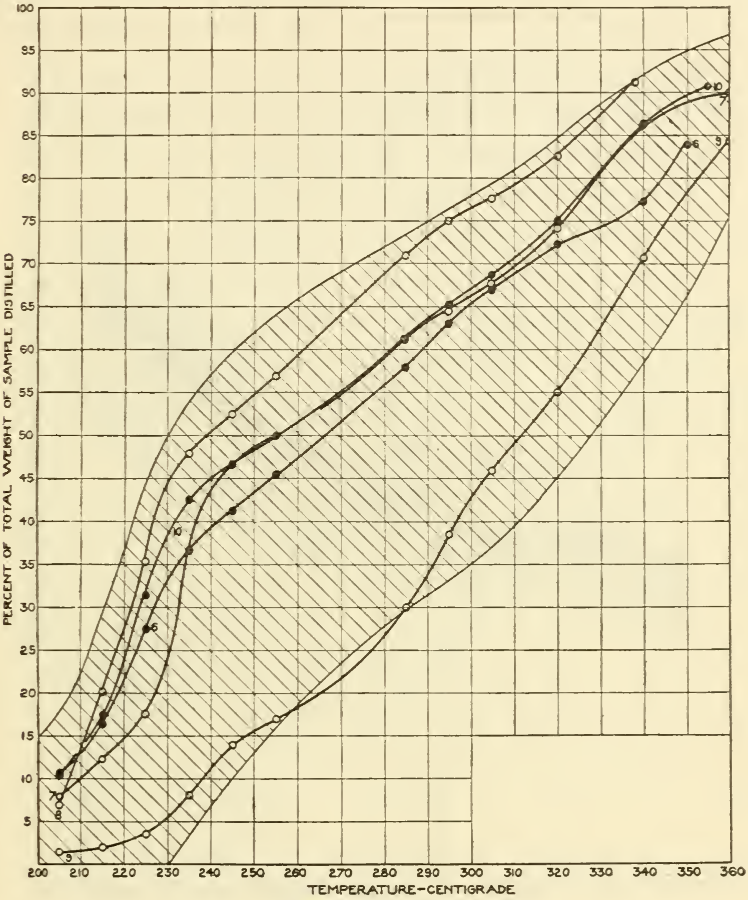

FIG. 7.—Fractional distillation curves for samples classified as mixed coal-tar creosotes (class 1).

From these results it was possible to divide the creosotes which were examined into several classes according to their properties. A classification adapted from that given in Circular 112 is here tentatively proposed.[1]

Coal-tar creosotes.

Coal-tar creosotes consist almost entirely of aromatic compounds, but are divided into two classes, according to the relative proportion of high and low boiling constituents. Their characteristic properties are as follows:

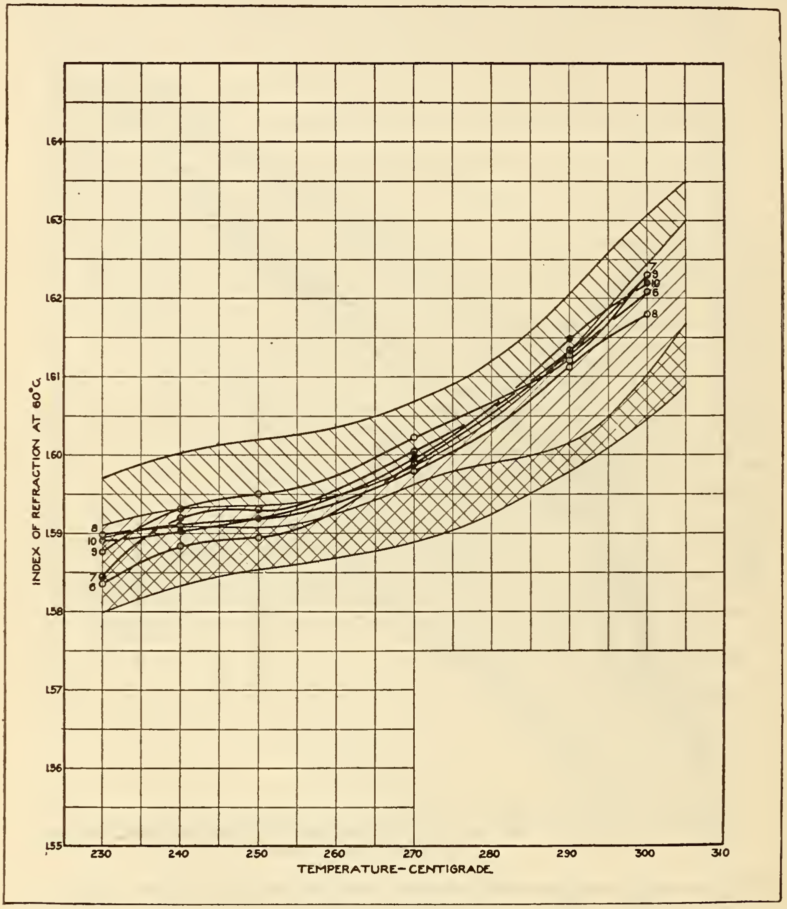

Fig. 8.—Index of refraction curves for samples classified as mixed coal-tar creosotes (class 1).

Class 1.—On a fractional distillation[2] the distillation curves fall within the lower shaded area shown in figure 5 (p. 15). The indices of refraction at 60° C. of the fractions do not fall more than one in the third place of decimals below the upper shaded area in figure 6 (p. 16), and the specific gravities at 60° C. do not fall more than one in the third place of decimals below the lower limit shown in figure 4 (p. 14). On applying the sulphonation test to the fractions between 305° and 320° C. there is no oily residue insoluble in caustic alkalies. The water does not exceed 1 per cent. There is no admixture of undistilled tar.

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[1] The classification has been slightly modified so that it will coincide with the definitions given in the first part of this publication. The third class, under mixed coal-tar creosotes, was not given in Circular 112.

[2] The method by which this distillation was made is described in the appendix.

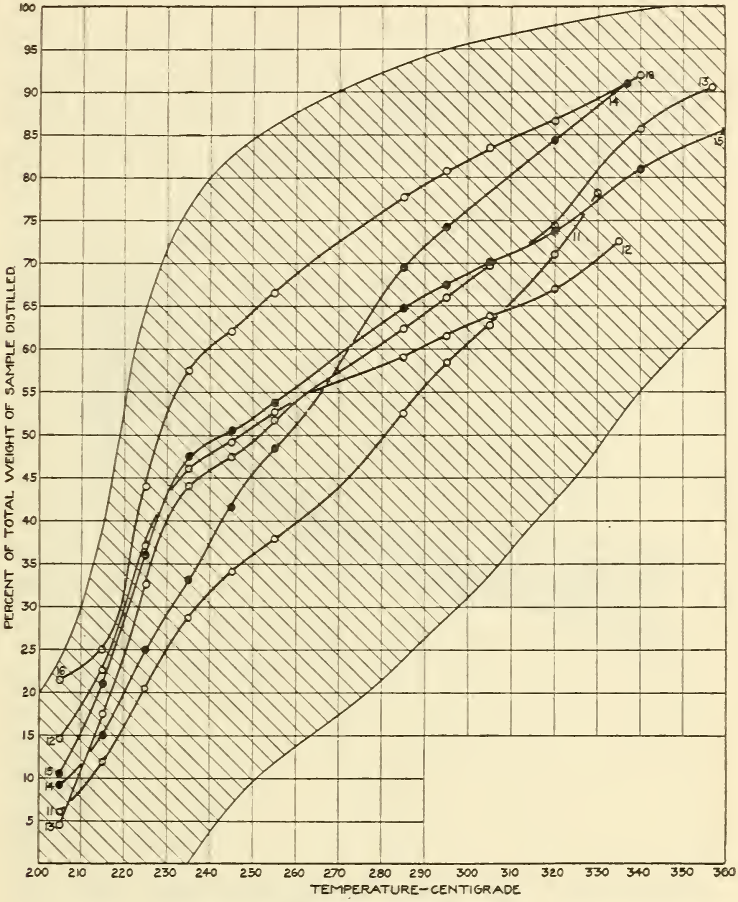

FIG. 9.—Fractional distillation curves for samples classified as mixed coal-tar creosotes (class 2).

Class 2.—The percentage weights on distillation fall within the upper shaded area shown in figure 5. The specifications for index of refraction, specific gravity, and sulphonation test are the same as for class No. 1. The water does not exceed 2 per cent. There is no admixture of undistilled tar.

Mixed coal-tar creosotes.

Mixed coal-tar creosotes are divided into three classes, according to the character and quantity of the admixtures.

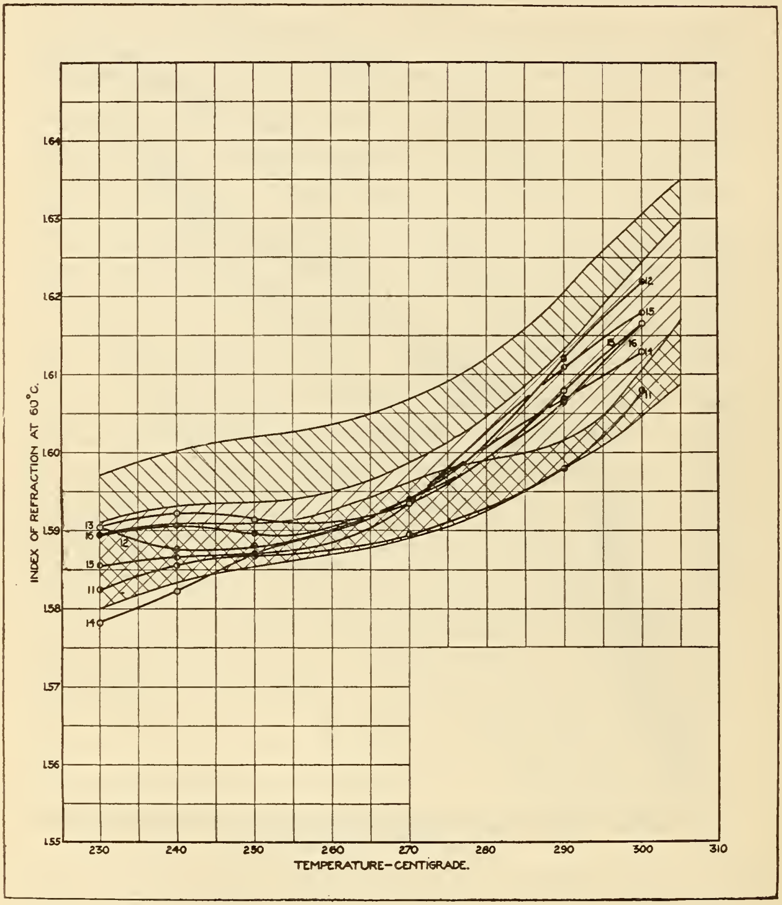

FIG. 10.—Index of refraction curves for samples classified as mixed coal-tar creosotes (class 2).

Class 1.—The presence of a certain amount of oil-tar creosote or products of a similar nature is admissible. The percentage weights on distillation fall within the shaded area shown in figure 7 (p. 17), and the indices of refraction fall within the middle shaded area shown in figure 8 (p. 18). The volume of the sulphonation residue, in cubic centimeters, from the fractions, at from 305° to 320° C., is not greater than one-tenth of the weight of the fraction in grams. The water does not exceed 4 per cent. There is no admixture of undistilled tar.

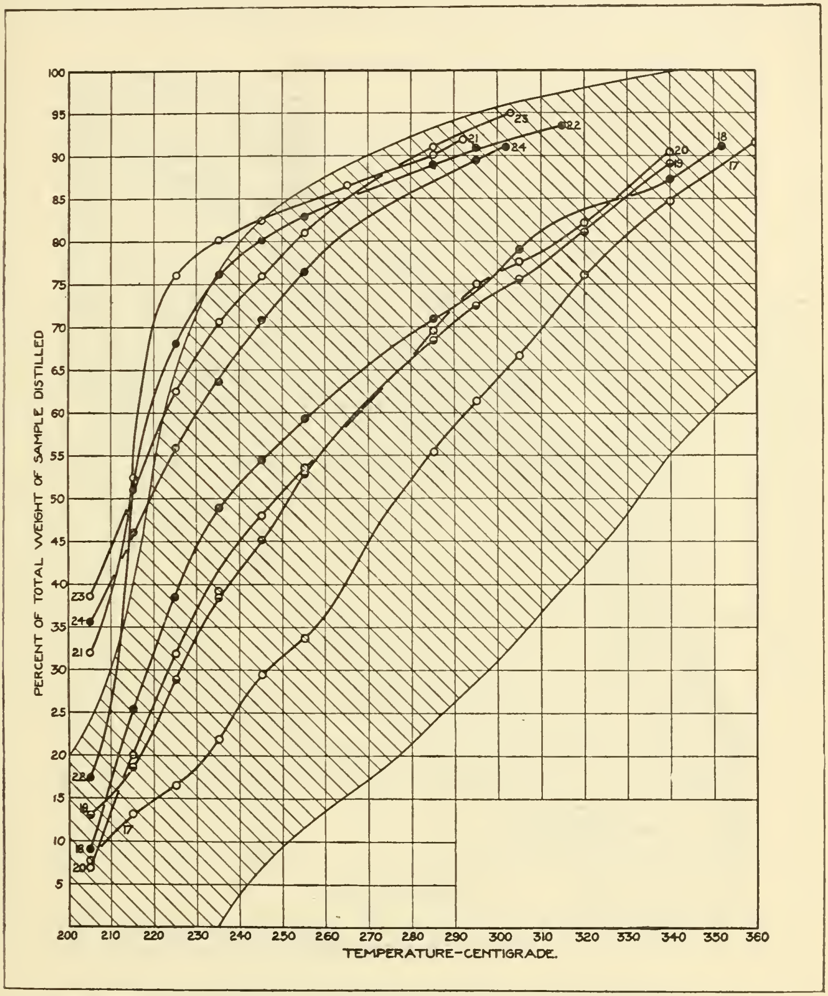

FIG. 11.—Fractional distillation curves for samples classified as mixed coal-tar creosotes (class 3).

Class 2.—Not only is the presence of certain quantities of oil-tar creosote or products of a similar nature admissible, but also adulterations with undistilled tar or other viscous material. The percentage weights on distillation fall within the shaded area shown in figure 9

(p. 19), and the indices of refraction fall within the lower shaded area shown in figure 10 (p. 20). The volume of the sulphonation residue, in cubic centimeters, from the fractions, at from 305° to 320° C., does not exceed one-fifth of the weight of the fraction in grams. The water in the creosote does not exceed 5 per cent, and admixture of undistilled tar or other viscous material does not exceed 15 per cent.

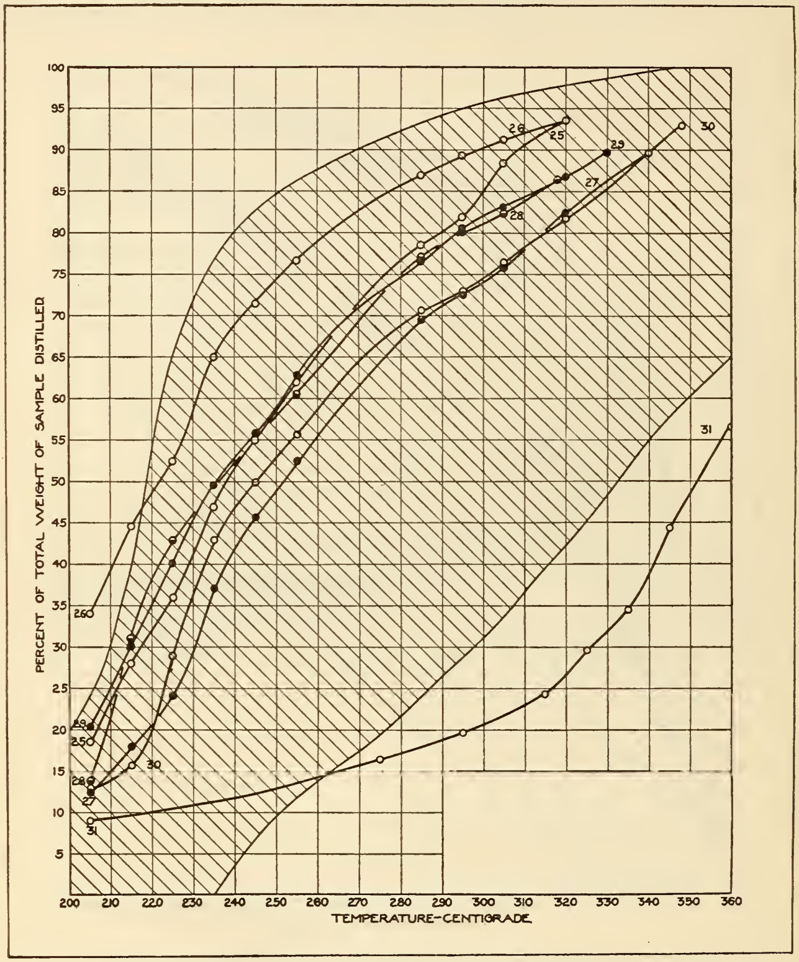

FIG. 12.—Fractional distillation curves for samples classified as mixed coal-tar creosotes (class 3) and water-gas-tar creosotes.

Class 3.—Mixed coal-tar creosotes which, on account of the quantity of paraffin constituents or undistilled tar or other viscous material present, can not be classified in either of the foregoing classes are included in this class. The properties of such mixtures vary so greatly, according to the nature of the constituents, that they admit of no general description.

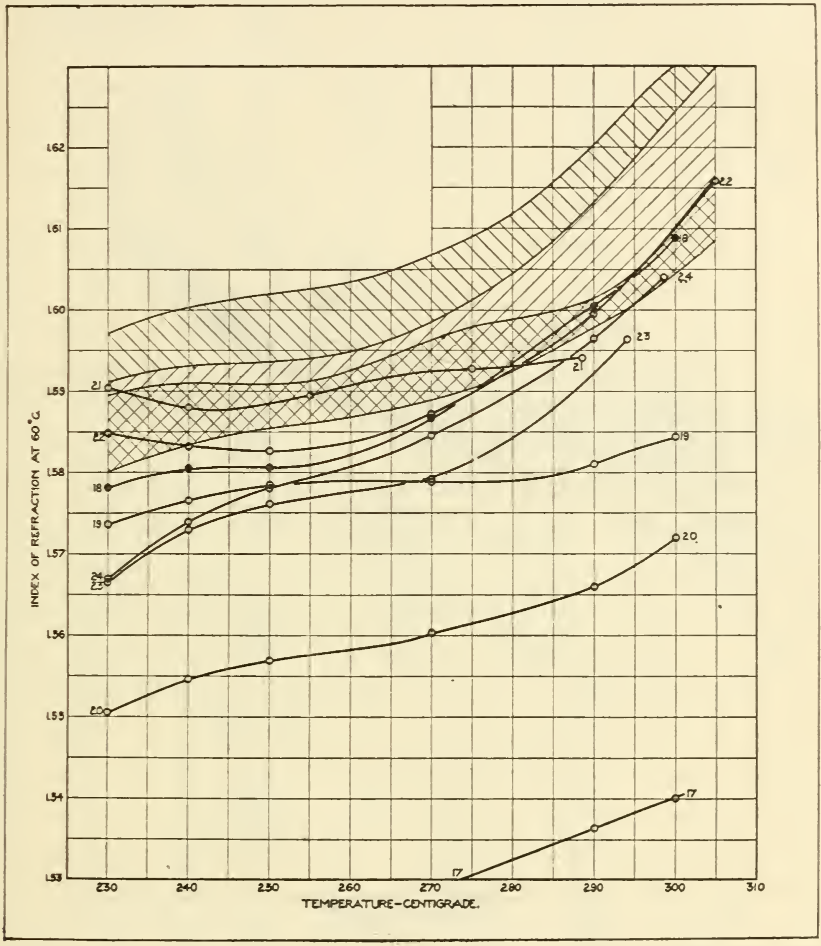

FIG. 13.—Index of refraction curves for samples classified as mixed coal-tar creosotes (class 3).

QUALITY OF COMMERCIAL CREOSOTES.

To secure authentic information on the quality and prices of available creosotes, the Forest Service, during 1909 and 1910, sought information and samples from a large number of dealers and manufacturers. In most cases these were supplied, and more than 70 per cent of the firms responded to the request for samples for analysis. No wood-tar creosotes were included.

All of the samples received were analyzed and classified, so far as possible, in accordance with the method described. The data secured from each sample are given in detail in Table 1 and in figures 5 to 14, inclusive. Although the method of examination is not entirely conclusive, all the samples were classified by the same method, and the results ought to give a fair comparison of the characteristics of the various samples.

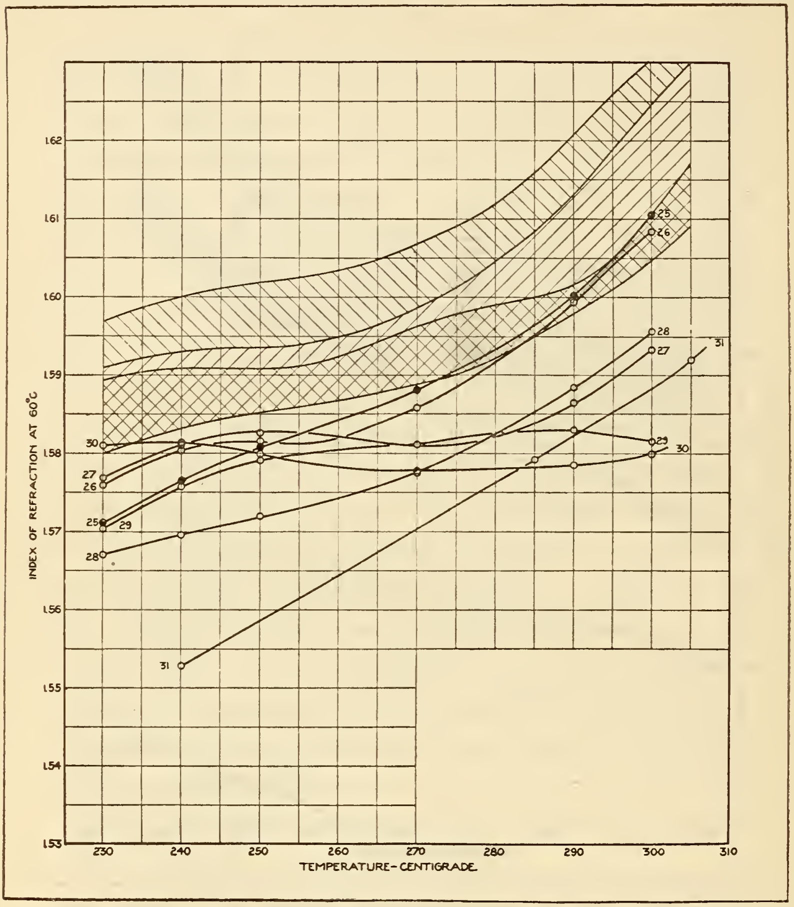

FIG. 14.—Index of refraction curves for samples classified as mixed coal-tar creosotes (class 3) and water-gas-tar creosotes.

Table 1.—*Classification and description of samples of commercial creosotes.*

Sample No.	Character of the oil.					Character of the fractions.			Character of residue.			Sulphonation residues of fractions, volume of residues (cubic centimeters) given in per cent of weight of fractions in grams.		
	Classification.	Color.	Odor.	Condition at room temperature.	Specific gravity at 60° C.	Distillation limits (°C.).	Color.	Condition at room temperature.	Temperature limits of distillation (°C.).	Color.	Condition.	Fraction 285°–295° C.	Fraction 295°–305° C.	Fraction 305°–320° C.
1	Coal-tar creosote, class 1.	Rich brown.	Not distinctive	Viscous liquid.	1.1158	To 305	Reddish	Liquid	360	Dark brown.	Crystalline paste.	([1])	([1])	([1])
						305–320	Dark brown.	Paste						
						320–340	Brown	Solid						
						340–360	do	Viscous liquid.						
2	do	Brown	Like that of naphthalene.	Liquid	1.0576	170–205	Pink	Paste	360	([2])	Viscous liquid	([1])	([1])	([1])
						205–225	do	Solid						
						225–235	Yellow	Paste						
						235–295	do	Liquid						
						295–320	do	Solid						
						320–360	Brown	do						
3	do	Greenish brown.	Decidedly like that of naphthalene.	Partially solid.	1.0533	To 205	Yellow	Liquid	340	Brownish black.	Would not flow at 60° C.	([1])	([1])	([1])
						205–245	White	Partially solid.						
						245–295	Yellow	Liquid						
						Above 295	Yellowish to yellow brown.	Partially solid.						
4	do	Brown	Not distinctive	Liquid	1.1118	205–245	White to yellow.	Solid	360	do	Clear liquid	([1])	([1])	([1])
						245–305	Bright yellow.	Liquid						
						305–340	Yellow	Solid						
						Above 340	Brown	Liquid						

[1] Too small to be regarded.

[2] Observation not recorded.

TABLE 1.—*Classification and description of samples of commercial creosotes*—Continued.

Sample No.	Character of the oil.					Character of the fractions.			Character of residue.			Sulphonation residues of fractions, volume of residues (cubic centimeters) given in per cent of weight of fractions in grams.		
	Classification.	Color.	Odor.	Condition at room temperature.	Specific gravity at 60° C.	Distillation limits (°C.).	Color.	Condition at room temperature.	Temperature limits of distillation (°C.).	Color.	Condition.	Fraction 285°–295° C.	Fraction 295°–305° C.	Fraction 305°–320° C.
5	Coal-tar creosote, class 2.	Brown......	Decidedly like that of naphthalene.	Partially solid.	1.0305	To 170	Clear yellow.	Liquid....	320	Black.......	Crystalline paste.	(1)	(1)	(1)
						170–235	White to yellow.	Partially solid.						
						235–295	Yellowish green.	Liquid....						
						Above 295	Green to orange.	Partially solid.						
6	Mixed coal-tar creosote, class 1.	.....do......	Like that of naphthalene.	Liquid....	1.0524	170–205	Yellow......	Liquid....	350	(2)	(2)	3.90	3.10	1.40
						205–215	.....do......	Paste.....						
						215–235	Yellowish	Solid......						
						235–295	Greenish yellow.	Liquid....						
						295–305	.....do......	Paste.....						
						305–320	.....do......	Solid......						
						320–350	Orange......	Paste.....						
7	.....do........	.....do......	.....do.............	...do......	1.0520	170–225	Straw color.	Liquid....	360	Black.......	Viscous liquid	7.00	3.90	1.80
						225–235	Yellow white or green.	Solid......						
						235–295	Yellow green.	Liquid....						
						Above 295	Yellowish green to orange.	Partially solid.						
8	.....do........	.....do......	Decidedly like that of naphthalene.	...do......	1.0303	205–235	White......	Solid......	338	Brownish black.	Soft paste....	....	2.90	2.50
						235–305	Yellow......	Partially liquid.						

						Above 305	Yellow green to brown green.	Solid						
9	do	Rich brown	Not distinctive	do	1.0996	To 170	Yellow	Liquid	360	(²)	Hard pitch	None.	None.	2.70
						170-205	Red	Paste						
						205-235	Pink	Solid						
						235-255	Brown	Liquid						
						255-305	Dark brown	do						
						305-340	Brownish yellow.	Solid						
						340-360	do	Liquid						
10	do	Dark brown	Like that of naphthalene.	do	1.0512	To 170		do	340	Brownish black.	Stiff paste	5.70	11.50	3.20
						170-245	White to yellow.	Partially solid.						
						245-285	Orange	Liquid						
						Above 285	Green to orange.	Partially solid.						
11	Mixed coal-tar creosote, class 2.	Rich brown black.	do	Viscous liquid.	1.0676	To 215	Red	Liquid	330	(²)	Soft	(³)	(³)	(³)
						215-225	Yellow	Solid						
						225-235	Yellowish brown.	do						
						235-295	do	Liquid						
						295-305	Green	Paste						
						305-320	do	Solid						
						320-330	Orange	do						
12	do	Black	Decidedly like that of naphthalene.	do	1.0747	205-235	Yellow white.	do	335	Bright luster.	Medium hard pitch.	(¹)	(¹)	(¹)
						235-285	Yellowish	Liquid						
						285-305	Brownish yellow.	Paste						
						305-335	do	Solid						
13	do	Brown	Like that of naphthalene.	Liquid	1.0371	To 170	Clear	Liquid	357	Brown	Paste		.20	1.00
						170-205	Yellow	Paste						
						205-215	Pink	Solid						
						215-225	Red	do						
						225-235	Brownish	do						
						235-245	do	Paste						
						245-295	do	Liquid						
						295-305	Green	Paste						
						305-340	Greenish brown.	Solid						
						340-357	Orange brown.	Paste						
14	do	do	Not distinctive	do	1.0371	To 305	White to reddish yellow.	Liquid	337	do	Soft paste	4.30	4.90	4.60
						305-337	Yellow	Solid						

[1] Too small to be regarded.

[2] Observation not recorded.

[3] No sulphonation tests.

TABLE 1.—*Classification and description of samples of commercial creosotes*—Continued.

Sample No.	Character of the oil.					Character of the fractions.			Character of residue.			Sulphonation residues of fractions, volume of residues (cubic centimeters) given in per cent of weight of fractions in grams.		
	Classification.	Color.	Odor.	Condition at room temperature.	Specific gravity at 60° C.	Distillation limits (°C.).	Color.	Condition at room temperature.	Temperature limits of distillation (°C.).	Color.	Condition.	Fraction 285°–295° C.	Fraction 295°–305° C.	Fraction 305°–320° C.
15	Mixed coal-tar creosote, class 2.	Black	Decidedly like that of naphthalene.	Liquid	1.0514	205–235	White to yellow.	Solid	360	Black	Solid	10.10	7.40	......
						235–285	Yellow	Liquid						
						285–305	do	Paste						
						305–340	Yellow green	Solid						
						340–360	Orange red	Paste						
16	do	Brownish black.	Like that of naphthalene.	do	1.0167	205–235	Pink to yellowish.	Solid	340	Brownish black.	Soft paste	6.20	2.30	4.20
						235–295	Yellow	Liquid						
						295–305	Yellow green	Paste						
						305–340	do	Solid						
[1] 17	Mixed coal-tar creosote, class 3.	Brown	Like that of crude petroleum.	do	.9657	170–360	Green to red.	Liquid	360	Black	Viscous liquid.	(2)	(2)	(2)
18	do	do	Like that of naphthalene.	do	1.0384	205–235	Yellowish	Solid	340	Dark brown.	Viscous paste.	3.60	2.90	3.30
						235–245	do	Thin paste						
						245–295	Orange	Liquid						
						295–350	Green	Solid						
19	do	Brownish black.	Like that of oil tar.	do	.9944	170–225	Yellow	Liquid	340	Brownish black.	Liquid	......	1.60	4.60
						225–235	White	Thin paste						
						235–305	Green to orange green.	Liquid						
						305–320	Green	Thin paste						
						320–340	do	Solid						
[3] 20	do	Brown	Like that of petroleum.	do	.9852	170–305	Yellow green	Liquid	340	Brown	do	(2)	(2)	(2)
						305–340	Green	Paste						
21	do	Brownish green.	Like that of naphthalene.	Half solid.	1.0092	170–205	......	Liquid	292	Black	Sticky paste.	(2)	(2)	(2)
						205–235	White to yellow.	Solid						

						235–292	Brownish yellow.	Liquid					
22	do	Brown	do	Solid		170–205	Yellow to red	do	315	do	Granular			[4] 3.50
						205–225	Yellow	Solid					
						225–235	Orange	Paste					
						235–295	Reddish brown.	Liquid					
						295–315	Yellow	Paste					
23	do	do	Not distinctive	Liquid	1.0000	To 285	Yellowish	Liquid	303	do	Sticky paste.	(2)	(2)	(2)
						Above 285	Greenish yellow.	Solid					
24	do	Greenish brown.	do	do	.9929	170–302	Yellow	Clear liquid.	302	Brownish black.	do	(2)	(2)	(2)
25	do	do	do	do	1.0189	170–225	do	Liquid	320		Viscous liquid		7.50	
						225–245	do	Paste					
						245–295	do	Liquid					
						295–320	Yellow green	Solid					
26	do	do	do	do	1.0036	170–285	Yellow	Clear liquid.	320	Brownish black.	Does not flow.	1.00	.30	.30
						285–295	Green	Paste					
						295–320	do	Solid					
27	do	Green	Like that of oil tar	do	1.0007	170–205	Yellow	Liquid	340	do	Liquid	(2)	(2)	(2)
						205–235	White	Paste					
						235–305	Yellow	Liquid					
						305–340	do	Solid					
28	do	Greenish brown.	Not distinctive	do	1.0123	170–305	do	Liquid	305	Dark brown.	Soft paste	(2)	(2)	(2)
						305–318	Yellow green	Partially solid.					
29	do	Brown	do	do	1.0175	To 170	White	Liquid	330	Brownish black.	Sticky paste.	(2)	(2)	(2)
						170–225	Yellowish green.	do					
						225–235	Yellow	Paste					
						235–295	Green	Liquid					
						295–330	do	Solid					
30	Water-gas-tar creosote.	Greenish brown.	Like that of oil tar	do	1.0040	170–205	Yellow	Liquid	348	Black	Viscous liquid		6.90	3.50
						205–215	White	Paste					
						215–225	do	Solid					
						225–235	do	Paste					
						235–295	Yellow	Liquid					
						295–320	do	Paste					
						320–348	do	Solid					
31	do	Reddish green.	Like that of kerosene.	Mobile (?) liquid.	1.0580	185–295	Light brown	Liquid	378	Dark brown.	Liquid	(2)	(2)	(2)
						295–378	Yellow	do					

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[1] Tar-acid contents of fraction from sample No. 17: 170°–245° C., very high in tar acids; 245°–255° C., 22 per cent; 255°–285° C., 16.7 per cent.

[2] No sulphonation tests.

[3] Tar-acid contents of fractions from sample No. 20: 170°–205° C., 1.5 per cent; 205°–215° C., 7.2 per cent; 215°–225° C., 7.3 per cent; 225°–235° C., 2.7 per cent; 235°–245° C., 3.4 per cent; 245°–255° C., 1.2 per cent; 255°–285° C., 0 per cent; 285°–295° C., 0.6 per cent; 295°–305° C., 0.4 per cent.

[4] For fraction 295°–315°.

The reason for putting each creosote in the particular class to which it is assigned will, in most cases, be apparent, but the following explanations are required as to certain of the samples:

Sample No. 1.—Although the index of refraction values of sample 1 fall practically within the limits assigned to coal-tar creosotes, the distillation curve falls somewhat below the limits assigned to such creosotes. The analysis seems to indicate that, although the sample was a coal-tar creosote, some of the lower-boiling constituents had been removed.

Sample No. 4.—The index of refraction values for the higher fractions of sample 4 have a tendency to fall below the limits assigned to coal-tar creosotes, which indicates that the sample may have contained a small admixture of a high-boiling petroleum substance. The distillation curve indicates that, as with sample 1, some of the lower-boiling constituents had been removed.

Samples Nos. 17 and 20.—The low index of refraction values of samples 17 and 20, in conjunction with the high tar-acid content of some of the fractions, indicate that these samples were from creosotes produced from blast-furnace tar.

Samples Nos. 30 and 31.—Samples 30 and 31 were known to be from creosotes produced from water-gas tar; their fractional distillation and indices of refraction are plotted in conjunction with the mixed coal-tar creosotes merely for convenience in comparison.

Samples Nos. 27, 28, and 29.—The similarity of the index of refraction values of samples 27, 28, and 29 to those of samples 30 and 31 leads to the belief that they also were water-gas-tar creosotes.

Table 2 is a classified summary, by regions of supply. It is interesting to note that of 31 samples of creosote received from all parts of the country, only 5 samples, or less than 17 per cent, could be classified as coal-tar creosotes, while approximately 80 per cent were graded as mixed coal-tar creosotes. The 2 remaining samples were known to have been produced from water-gas tar. Of the 5 samples graded as coal-tar creosotes, 2 were supplied from the East, 2 from the South, and 1 from the Middle West.

TABLE 2.—*Classification of samples of commercial creosotes.*

[Actual number and per cent of total falling in each class.]

Region.	Number of firms which submitted samples.	Number of samples submitted.	Coal-tar creosotes.						Mixed coal-tar creosotes.									Water-gas-tar creosotes.		
			Class 1.			Class 2.			Class 1.			Class 2.			Class 3.					
			Sample No.	Number.	Per cent.	Sample No.	Number.	Per cent.	Sample No.	Number.	Per cent.	Sample No.	Number.	Per cent.	Sample No.	Number.	Per cent.	Sample No.	Number.	Per cent.
Eastern States........	7	10	3	1	10	5	1	10	....	0	0	12	1	10	19, 20, 21, 26, 27	5	50	30, 31	2	20
Southern States.......	6	11	1, 2	2	18.2	....	0	0	6, 7, 9, 10	4	36.4	11, 13, 15	3	27.2	17, 18	2	18.2	....	0	0
Middle Western States.	5	5	4	1	20	....	0	0	8	1	20	16	1	20	22, 23	2	40	....	0	0
States west of the Mississippi River.......	5	5	....	0	0	....	0	0	....	0	0	14	1	20	24, 25, 28, 29	4	80	....	0	0
Total...........	....	31	....	4	13	....	1	3	....	5	16	....	6	19	....	13	42	....	2	7

PRICES AND CONSUMPTION.

The quoted prices per gallon f. o. b. works are summarized in Table 3. It is only fair to state that the high quotations in the maximum columns under "Middle Western States" were all received from one firm and apply to what is said to be a special grade of oil. It is unfair, therefore, to compare these quotations with the others and the next high quotations have been inserted in brackets in these columns.

A comparison of the individual figures reveals the fact that in all sections of the country the price for small lots is considerably in excess of that for large orders or tank-car lots; increase in individual cases varies from 25 to 200 per cent. In practically all cases the quotations from the Eastern States were lower than for the other sections. In general they differed but slightly from the quotations from the Southern and Middle West sections, yet there is a decided difference when compared to the States west of the Mississippi River. The low minimum quotations for tank-car lots in the States west of the Mississippi River apply to the Pacific coast; in the Rocky Mountain region higher prices prevail as a result of the heavy freight charges on creosote shipped to these points.

Similar statistics were not collected for wood-tar creosotes, but the price for small orders is likely to be from 40 to 60 cents per gallon. It is possible that in large quantities wood-tar creosote may be secured at a considerably lower figure.

TABLE 3.—*Prices of commercial creosotes.*

Region.	Number of firms addressed.	Price per gallon f. o. b. works, including package.								
		1-barrel orders.			60-barrel orders.			Tank-car lots.		
		Number of quotations.	Maximum.	Minimum.	Number of quotations.	Maximum.	Minimum.	Number of quotations.	Maximum.	Minimum.
			Cents.	*Cents.*		*Cents.*	*Cents.*		*Cents.*	*Cents.*
Eastern States	13	5	15	7	5	12	7.5	5	12	5.5
Southern States	9	5	20	9	3	16	12	6	12	6.7
Middle Western States	7	4	[1] 60 [20]	12	3	[1] 40 [12]	10	4	[1] 40 [9]	5.5
States west of the Mississippi River	7	5	25	20	4	19	16	4	15	[2] 6.7

[1] These figures apply to what is said to be a special grade of oil. Figures in brackets are next highest quotations received.

[2] This low quotation is from a firm on the Pacific coast, and applies to an imported product.

Statistics of the consumption of commercial creosotes do not as a rule distinguish between coal-tar creosotes and other closely allied products. However, coal-tar creosotes, either pure or more or less mixed with other products, make up the bulk of the consumption, and the figures given in Table 4 may therefore be taken to represent the approximate quantity of these creosotes used. It is probable that a small amount of oil-tar creosote also is included in the figures.

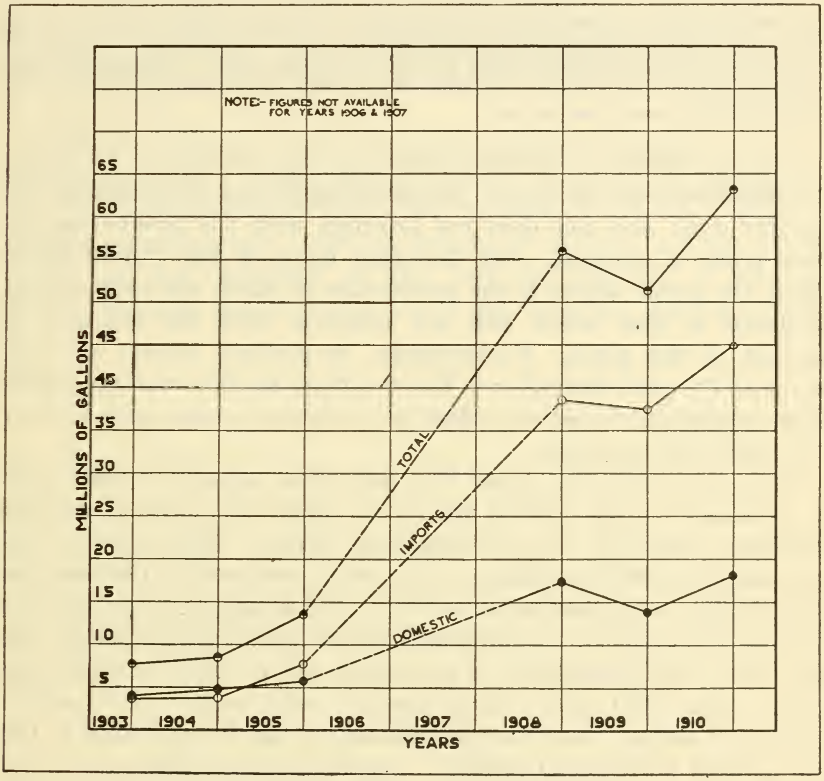

FIG. 15.—Consumption of creosotes in the United States.

The statistics are represented diagrammatically in figure 15, which shows the strikingly rapid increase in the consumption of creosote, as well as the relatively small quantity produced in this country. In 1903 and 1904 the domestic production exceeded the imports, but since that time, although the annual consumption of domestic creosote has practically quadrupled, the imports have rapidly outstripped the domestic production, and in 1910 exceeded it by almost 150 per cent.

TABLE 4.—*Consumption of creosotes.*

Year.	Domestic.	Imported.	Total.
	Gallons.	*Gallons.*	*Gallons.*
1903 [1]	4,000,000	3,711,565	7,711,565
1904 [1]	4,850,000	3,783,472	8,633,472
1905 [1]	5,800,000	7,750,531	13,550,531
1908 [2]	17,360,000	38,640,000	56,000,000
1909 [2]	13,862,171	37,569,041	51,431,212
1910 [2]	18,184,355	45,081,916	63,266,271

[1] The figures for 1903, 1904, and 1905 were taken from Forest Service Circular 98, and apply to coal-tar creosote. The domestic supply figures are from estimates by Prof. Gellert Alleman. Imports are from the annual reports of the Department of Commerce and Labor.

[2] The figures for 1908, 1909, and 1910 are from Forest Service Circular 185 and were compiled from reports on the consumption of creosote received from more than 90 per cent of the treating plants in operation during these years.

No figures are available for 1906 and 1907.

It is not difficult to find the reason for this condition. In Europe the refinement of coal tar is conducted largely for the production of coal-tar dyes, and this does not interfere with the production of a good grade of creosote. On the other hand, in the United States' where the prime object is the production of pitch, the only creosote produced is that which will not interfere with the character or amount of the pitch. Furthermore, by-product retorts are more extensively used throughout Europe than in this country, where large quantities of coal are coked in the beehive ovens with a loss of the possible by-products.

There is no reason to doubt that more than enough creosote might be produced in the United States to supply the present demand. Statistics published by the Geological Survey [1] show that in 1909 practically 60,000,000 gallons of tar were produced in the manufacture of coke in by-product coke ovens, and although no statistics are at hand showing the tar produced at the gas-house plants for that year the total production of gas-house tar in 1907 and 1908 was greater than that from the by-product coke ovens. It is safe to assume, therefore, that the total amount of coal-tar produced in 1909 was at least 100,000,000 gallons. Assuming that 5 gallons of tar will produce 1 gallon of creosote, the total amount of coal-tar creosote which might have been produced is approximately 20,000,000 gallons, or about 50 per cent more than the domestic creosote consumed that year. This possible production could be further vastly increased by the wider use of the by-product retorts. The average yield of tar from the bituminous coal coked in the by-product ovens in 1909 was 6.4 gallons per short ton; the approximate quantity of bituminous coal coked in the bee-hive ovens during that year was 51,000,000 short tons. Had this coal been coked in by-product ovens, approximately 326,000,000 gallons of tar might have been produced, or an amount sufficient to provide more than 65,000,000 gallons of coal-tar creosote. This amount exceeds the total consumption for that year by more than 13,500,000 gallons.

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[1] All statistics quoted from the Geological Survey are taken from the following publications: The Manufacture of Coke in 1909, by Edward W. Parker, and Production of Gas, Coke, Tar, and Ammonia at Gas Works and in Retort Coke Ovens, and of Gas and Tar at Water-Gas Works, by the same author.

The Geological Survey reports the production of 9,168,834 gallons of oil and water-gas tars in 1908, but the report states that "most of the tar is used for fuel at the works, no record being kept of the output." Substantiating this theory, it is then stated that "in addition to the amount above listed over 5,500,000 gallons were reported in 1908 as made and not sold." Only recently has oil-tar creosote been marketed under that name. Statistics of the production or consumption are not available, but it is undoubtedly much in excess of the figures given.

Wood-tar creosotes do not at present rank in importance with the coal-tar creosotes. Although the quantity of wood tar produced in 1909 was approximately 20,000,000 [1] gallons, an amount capable of yielding approximately 2,000,000 gallons of creosote, a large portion of this tar was consumed as fuel, and the quantity of wood-tar creosote actually produced was much less than the possible production.

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[1] This figure is estimated from statistics published by the Bureau of the Census in Wood Distillation, 1909.

APPENDIX.

METHOD USED IN ANALYZING THE CREOSOTES DISCUSSED IN THIS PUBLICATION.[1]

[NOTE.—All temperatures referred to in the following are on the centigrade scale.]

Specific gravity of the whole oil.

The perfectly liquefied oil is poured into a hydrometer cylinder, and, at a temperature of 60°, the specific gravity is read with hydrometer standardized against water at 60°.

The somewhat prevalent method of determining specific gravity with a hydrometer standardized at 15° and then calculating the results from the temperature of the determination back to 15° is roundabout and involves the expression of the specific gravity of creosote in the liquid condition at a temperature at which the oil does not exist as a liquid. The method is illogical and open to inaccuracies. With very rare exceptions creosotes are all liquid at 60°, and if the weight of a unit volume of the oil at 60° is compared with the weight of a unit volume of water at 60°, a true specific gravity is obtained. * * *

Fractional distillation.

The Hempel distilling flask of resistance glass, shown in figure 16, is employed. The empty flask is tared, 250 grams of melted, well-shaken oil introduced, the platinum-wire plug and the glass beads put in place, and a second weight taken. The thermometer is then inserted in the flask, so that the first emergent reading is 200°.[2]

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[1] Condensed and reprinted from Forest Service Circular 112.

[2] In the distillations and analyses described in this publication, one thermometer standardized by the Bureau of Standards was used throughout and was in all cases inserted in the Hempel flask so that the bulb was opposite the outlet tube. The temperatures actually recorded by the thermometer were used in plotting the distillation curves and limits of the different classes of creosote. Corrections for the emergent stem of the thermometer were not made, as, using the same thermometer placed in the same position, the results will be constant within the limits of error in the methods employed. However, should it be desired to compare the analyses given in this publication with the analyses of other creosotes similarly distilled, using a standardized thermometer but calibrated to a different scale, so that the first emergent reading is not 200° C., the temperatures should be corrected in both cases. The correction to be added to the observed temperatures can be determined by the following formula:

$$\text{Correction}=0.00016(T-t)N,$$

where

T=thermometer reading.
t=temperature of emergent stem.
N=number of degrees of the thermometer reading which are emergent.

The following table gives the corrections which should be used for the results in this publication:

TABLE 1.—*Corrections for the emergent thermometer stem.*

Temperature reading.	Corrected reading.	Temperature reading.	Corrected reading.
°	°	°	°
170	170	250	251.6
180	180	260	262
190	190	270	272.4
200	200	280	282.9
210	210.3	290	293.4
220	220.6	300	303.9
230	230.9	310	314.4
240	241.2	320	325

The flask is supported on an asbestos board with a slightly irregular opening of very nearly the largest diameter of the flask. A condensing tube is employed and the fractions are collected in tared flasks. The distillation is run at the rate of 1 drop per second, and fractions collected between the following temperatures: Up to 170°, 170°–205°, 205°–225°, 225°–235°, 235°–245°, 245°–255°, 255°–285°, 285°–295°, 295°–305°, 305°–320°, and if feasible, 320°–360°.

The character of the fractions and their weights are recorded and the results plotted as a curve, in which the ordinates are percentages by weight and the abscissæ temperatures. * * * When the distillation has reached the 225° point, an asbestos-board box should be placed around the distilling flask, to cover the bulb, but leave the Hempel column exposed. Drafts upon the distilling apparatus must be avoided.

Index of refraction.[1]

The indices of refraction of the different fractions between 235° and 305° are determined at 60° in a refractometer with light compensation. The results are plotted with temperatures as abscissæ and indices of refraction as ordinates.

Specific gravity.

The specific gravities of the fractions between 235° and 305° are determined by means of specific-gravity bottles. These bottles are filled at 60° and the weights referred to water at the same temperature. The results are plotted as a curve, in which the ordinates are specific gravities at 60° and the abscissæ temperatures.

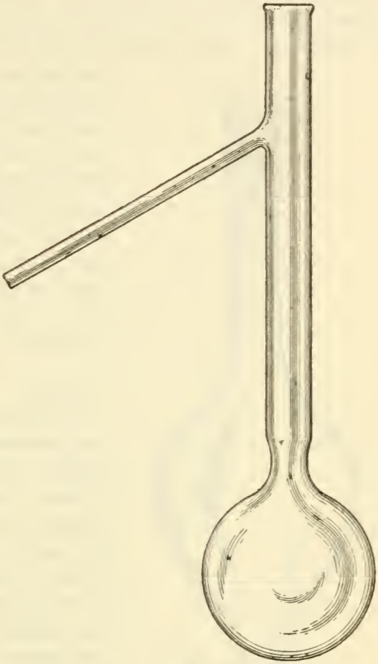

FIG. 16.—Hempel distilling flask.

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[1] The following explanation of the index of refraction and of the sulphonation test is also taken from Forest Service Circular 112:

"INDEX OF REFRACTION.

"The index of refraction is the ratio between the sines of the angles of incidence and of refraction of light, expressed by the formula $\frac{n}{D}=\frac{\text{sine I}}{\text{sine R}}$, where $\frac{n}{D}$ means the index of refraction referred to sodium light, I equals the angle of incidence, and R the angle of refraction. The index of refraction varies with the temperature, but is constant for any given oil at a stated temperature. In making measurements of the index of refraction of the different fractions of a creosote distillation, it was necessary to make the measurements at 60°. The determinations were made with an Abbe refractometer provided with a light compensator. By means of this instrument the index of refraction may be read with great accuracy, and the measurement is one of the most exact which can be applied to such an oil."

"SULPHONATION TEST.

"In contradistinction to the hydrocarbons of the paraffin series, those of the aromatic series react with concentrated sulphuric acid with marked ease. The products of this reaction, in which a sulpho group or groups replace hydrogen in the aromatic compound, are called sulphonic acids and the process is known as sulphonation. For example, the reaction with benzene would be $C_6H_6+H_2SO_4=C_6H_5SO_3H+H_2O$. The sulphonic acids are characterized by their solubility in water. If a fraction from the distillation of a creosote oil be treated under proper conditions with concentrated sulphuric acid, it will be converted into a mixture of sulphonic acids, which will readily dissolve in water. If, however, there are paraffin bodies present they will not be attacked to the same degree as the aromatic hydrocarbons, and when the products of the sulphonation are treated with water the paraffin components will remain as a residual oil. In applying this test to creosote oils it has been found that the most information is obtained by using it on the higher-boiling fractions."

Sulphonation test.

The fraction distilling between 305° and 320° is treated with concentrated sulphuric acid and poured into a separatory funnel such as is shown in figure 17. The flask which contained the fraction is rinsed out twice more with concentrated sulphuric acid and the rinsings added to the funnel. Enough more concentrated sulphuric acid is added nearly to fill the funnel, and the mixture is thoroughly shaken at least six times in 30 minutes. After standing until it becomes cool the volume is brought up into the graduations by the addition of concentrated sulphuric acid, and after another hour the amount of unsulphonated oil is read and the percentage calculated. The residual oil is usually almost white or a pale blue. In some cases a reddish oil with a distinctive odor is obtained from a pure coal-tar creosote; this oil does not consist of hydrocarbons and is soluble in caustic alkalies. The sulphuric acid should therefore be drawn off, the oil washed with water, and a 10 per cent solution of sodium hydroxide added. If the oil is soluble in this reagent, the sulphonation test is regarded as negative.[1]

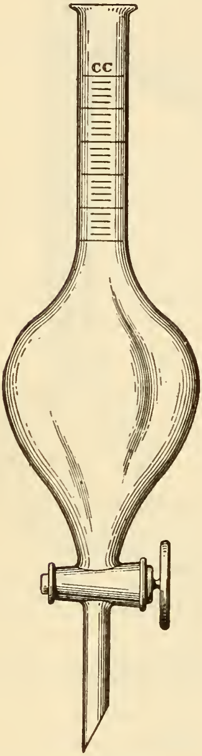

Fig. 17.—Separatory funnel for sulphonation test.

Tar acids.

Fifty cubic centimeters of the creosote under analysis are measured at 60° into a small distilling flask by a pipette. The oil is distilled as completely as possible without breaking the distilling bulb, and the distillate is caught in a short-stemmed, 100 cubic centimeter separating funnel. At the end of the distillation 25 cubic centimeters of boiling hot 15 per cent sodium hydroxide is added to the distillate and the mixture thoroughly shaken. The alkaline extract is then drawn off into a 100 cubic centimeter shaking cylinder and 25 cubic centimeters more of hot sodium hydroxide added. After extracting with this second portion for five minutes, with frequent shaking, the solutions are allowed to separate and the alkaline extract added to the first portion in the cylinder. A third extraction is made with 15 cubic centimeters of alkali. The total alkaline extract is cooled, acidified with sulphuric acid, thoroughly shaken, brought to 60°, and the volume of supernatant oil read off.

Water.

After weighing the first two fractions of a fractional distillation they are united in a small separatory funnel and any water which is present is separated from the oil and its amount accurately determined. If particular accuracy is required in the estimation of the water it may be done by the Marcusson xylol distillation method.[2]

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[1] More recent investigations have led to a modification of this method; described in Forest Service Circular 190, by Ernest Bateman.

[2] Forest Service Circular 134, The Estimation of Moisture in Creosoted Wood.

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